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A Study of the Character of Spent Liquor form the
Neutral [SIC] Sulfitc Semichemical Process of Pulping

Written by
Bob LeGault

INTRODUCTION:

The utilization of spent liquors has been a major item in the research and development field of the pulp and paper industry. In recent years, this problem is being given more serious emphasis due to the tightening of anti-pollution laws by government agencies. This situation, together with the individual mill's desire to find programs for sound and effective recovery of values are major recipients of engineering and research man hours and dollars. This all points towards a better future for the industry and the community. A closer study than just analysis and physical constants determination is undoubtedly needed in order to better define the path the spent liquor will or will not follow, ultimately leading to its commercial utilization.

BACKGROUND:

On several occasions in the past a certain company has been troubled by inconsistencies of the mill's NSSC spent liquor when electrodialed. The Sulphite Pulp Manufacturer's Research League (1) claims that the early batches of liquor sent for processing in the latter part of 1962 gave no problem as far as sludging or precipitation is concerned. On the contrary, most of the batches of liquor submitted in 1963 produced a significant quantity while being electrodialed, the result of which was undue plugging of the membranes.

A number of theories have been advanced to account for the differences:

1. At one time, it was thought to be the result of bacterial action resulting in the formation of thiosulfates.
2. It may also be possible to consider the presence of fine suspension consisting of no-length fibers, ray cells, waxy and gummy substances in the wood which are flocculated by lowering of the pH.
3. It has also been assumed that possibly sulfonation was incomplete thus precipitating alkali lignin when electrodialed.
4. Since the wood source consisted of a number of combinations of wood species it was thought that, possibly, the differences could be traced to a particular wood species.

There may be more of these theories that would account for this change.

It was thought that thin layer chromatography might offer a method for coarse separations of the major constituents in the spent liquors from individual wood species. A physical indication of this is shown in chromatograms through the colors imparted by the components when stained with certain

chromogenic substances. A chromatogram is developed by spotting a sample on a silica gel layer and letting the components migrate with a certain solvent depending upon their absorptivity in the layer. If the components are colored, they could be seen in the chromatograms after drying of the layer. Otherwise, a certain color imparting substance is sprayed on and after baking the resulting colors could be used as a basis for comparison. Qualification of thin layer chromatography as a method for such comparisons may be gained from the fact that the Sulphite Pulp Manufacturer's Research League and United States Forest Products Laboratory has seen fit to utilize it in a considerable amount of similar work.

OBJECTIVES:

A study was made of the behavior of NSSC spent liquor samples derived from the digestion of known wood species when subjected to thin layer chromatography. Thin layer chromatography was utilized as a basis of comparison and a preliminary means of ascertaining what degree of cooking had proceeded or not. The latter was shown by a big change in color intensity or an appearance of new colored spots.

EXPERIMENTAL PROCEDURE:

Preparation of liquor samples: Laboratory digestion approaching set conditions as close as possible was performed on the individual wood species of Hemlock, Aspen, White Birch, and Hard Maple. The initial liquor used in the digestions was made up of 10% sodium sulfite, 3% sodium carbonate, and 87% water by weight. The pH of this initial liquor averaged about 9.5. One hundred grams of oven dry wood and four hundred grams of the initial liquor were added to each of three flasks and impregnated for a half an hour. After the impregnation period the flasks were placed in the laboratory digester and cooked for four hours at a steam pressure of 25 p.s.i.g. or a temperature of 130° C.. After the cooking period the free liquor (that which could be drained off) was removed from the chips. With the aid of a Waring Blendor the liquor within the chips was removed and added to the free liquor. Sodium carbonate and sodium sulfite were added to this liquor in the ratio of 1:3 $\frac{1}{2}$, respectively, by weight until the pH was again in the range of 9.0 to 9.5. This refortified liquor was added to fresh chips and the cooking procedure continued. The whole process was repeated three times for each species. After the last digestion the spent liquor samples were collected and diluted to a uniform solids content of ten per cent. The pH of the final spent liquors ranged from 6.5 to 6.9.

Preparation of thin layer chromatography plates: Silica gel G was made into a slurry with water at a ratio of 13.5 grams powder and 25 ml. water. The water was added into the weighed powder in portions with the last 5 cc. in ml. amounts. This would take care of the weighing errors that may accidentally be made. The right consistency was arrived at with experience. The prepared slurry, which was enough for four big plates, was spread by an applicator

adapted for the purpose. The spreading was done without hesitation in order to prevent "breaks" along the layer length. This would have impeded the solvent travel while developing. The layered plates were then activated in the oven for about one hour.

Solvent preparation for thin layer chromatography: The solvent that was used consisted of ethanol, methanol, and water in the ratio of 50:80:4, respectively. The solvent was prepared ahead of time and placed in a sealed chromatogar lined with filter paper to insure complete saturation of the atmosphere inside the jar. It was found that a good amount of solvent for one trial was about 60 ml. and that the tank was usually well saturated after one hour of standing.

Spotting of spent liquor on the chromatogram: After the plates were cooled to "hand touch" temperature and the edges scraped off the layer, the samples were spotted onto the plates with the aid of a wooden template. This insured proper spacing of the sample spots and avoided overlapping of chromatograms. The sample was spotted with a drawn out glass tube producing as small a spot as possible and at the same time having enough material in it. A smaller spot was reported to have a better separation. This aspect of the sample application could only be well understood by several practice runs to get a better feel of how much is "enough".

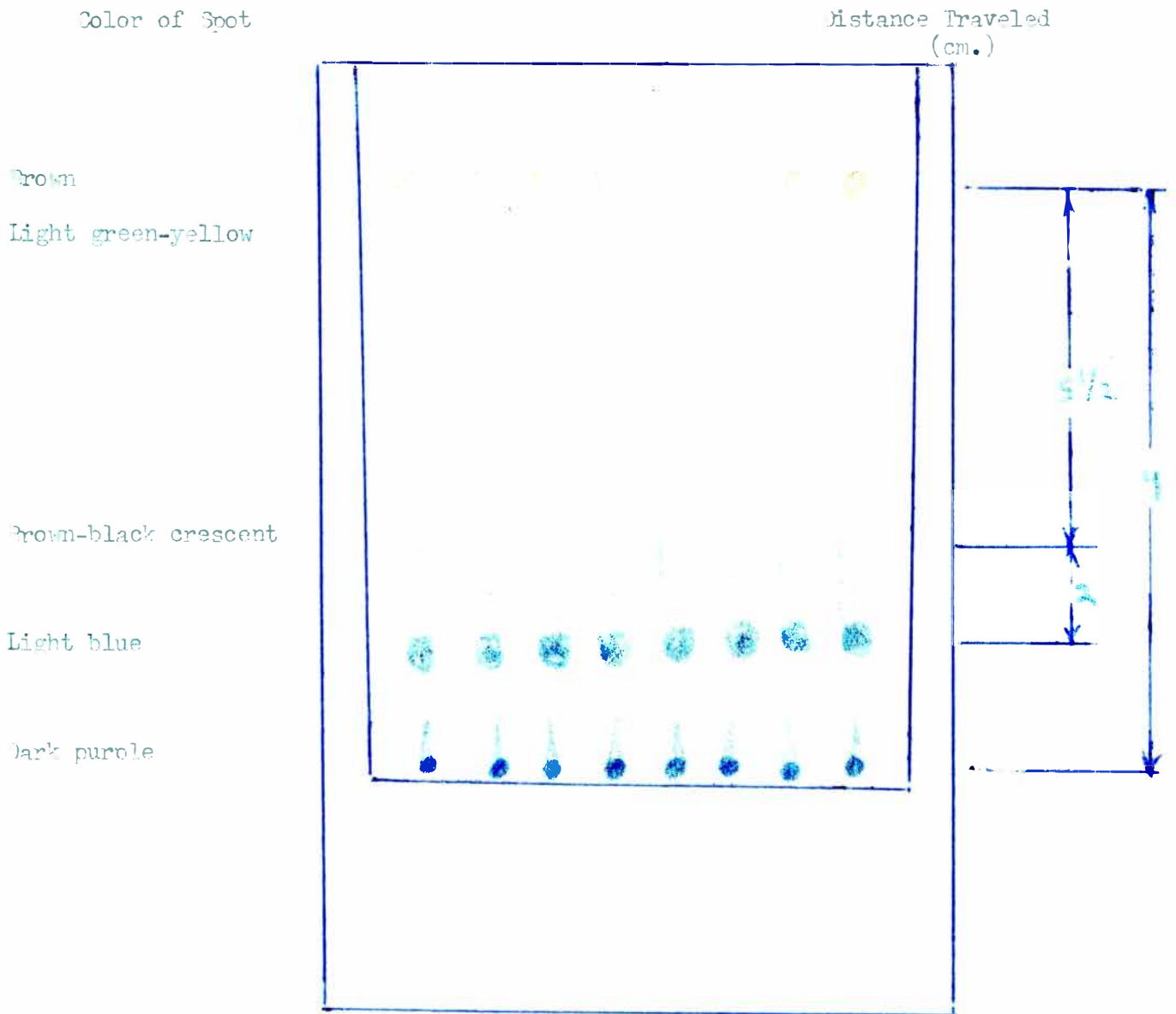
Developing the chromatograms: The spotted glass plates were then placed in the chromatogar and the lid replaced at once in order not to disturb the saturated condition of the atmosphere inside. The solvent front was then observed until it reached a predetermined line on the plate which was about 10 cm. from the starting line. Development was then stopped, the glass

plate picked up and set aside to drive off as much solvent as possible. At this stage, the components of the sample under investigation were brought up by the solvent at points depending upon their absorption characteristics in silica gel. In the particular case of M33C liquor, the components were colorless and had to be stained by a chromogenic mixture of anisaldehyde, glacial acetic acid, and concentrated sulfuric acid in the volumetric ratio of 1:97:2.

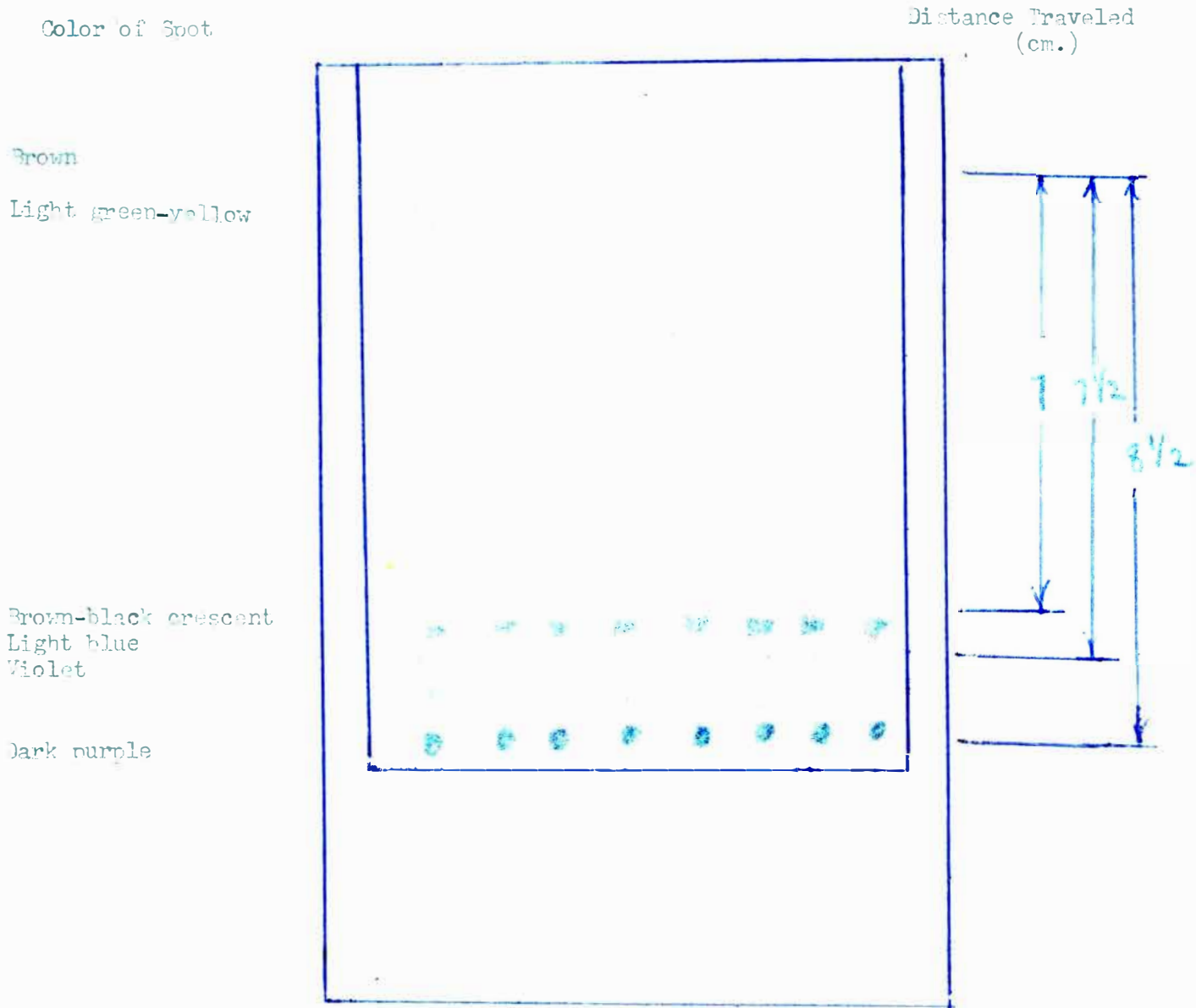
Staining the chromatograms: The staining mixture mentioned above had to be freshly prepared because of its instability especially to heat and light. About 20 ml. of the mixture was used up in spraying two pairs of 10 x 15 cm. glass plates. It has been observed that this mixture changes from colorless to yellow to orange and finally to red with time. Thus it is recommended that the mixture be used within three days after preparation to insure uniformity and good staining properties. Staining was done by spraying a plate several times with the above mentioned mixture. The spraying distance, the duration of the spraying and other details were, again, well understood by actual practice. After staining, the sprayed plates were baked in a 110° C. oven for five to ten minutes to bring out the colors. The colors were usually the sharpest when the baked plates were set aside to cool for about fifteen minutes. However, half a day to a day's standing in the air was enough to have the colors fade. So interpretations from the finished product were made within two to three hours.

Preservation of chromatogram results: It was felt that the results could be preserved for further evaluation and comparison by copying in a note book with the aid of colored pencils. Such results of the chromatograms are illustrated in the next pages.

Hamlock Chromatogram



White Birch Chromatogram I.



Hard Maple Chromatogram

Color of Spot

Distance Traveled
(cm.)

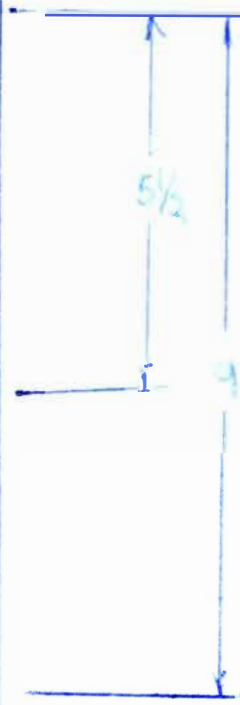
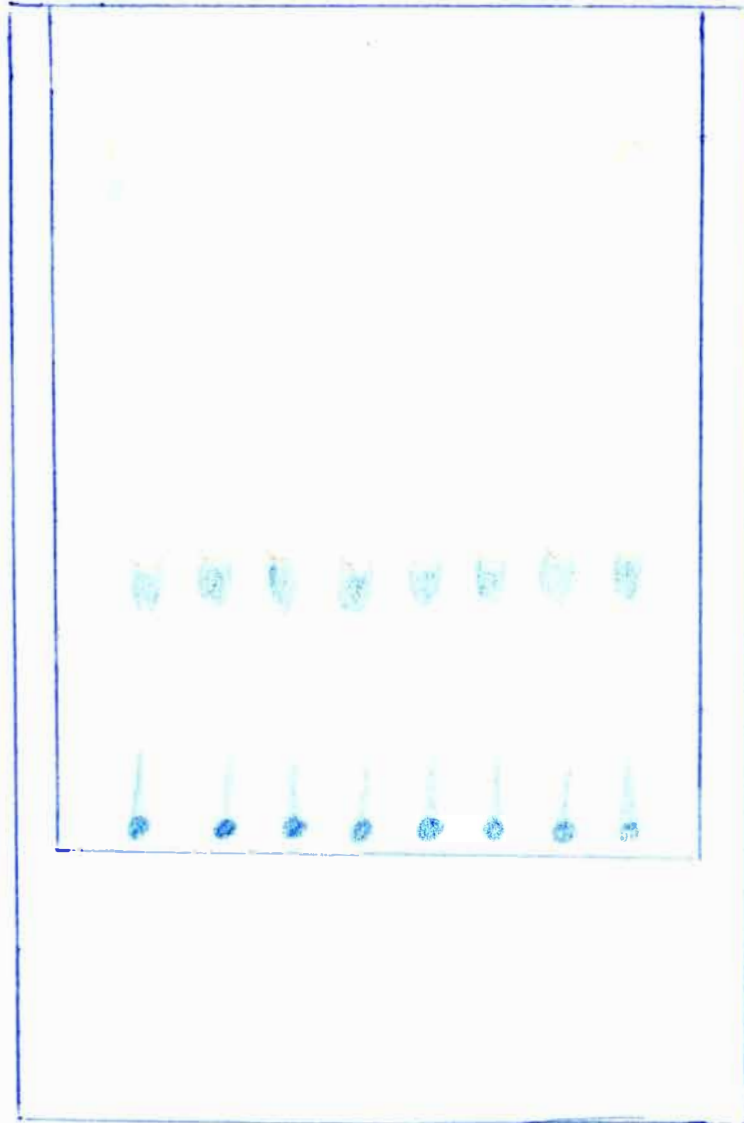
Brown

Light green-yellow

Brown-black crescent

Light blue

Dark purple



Aspen Chromatogram

Color of Spot

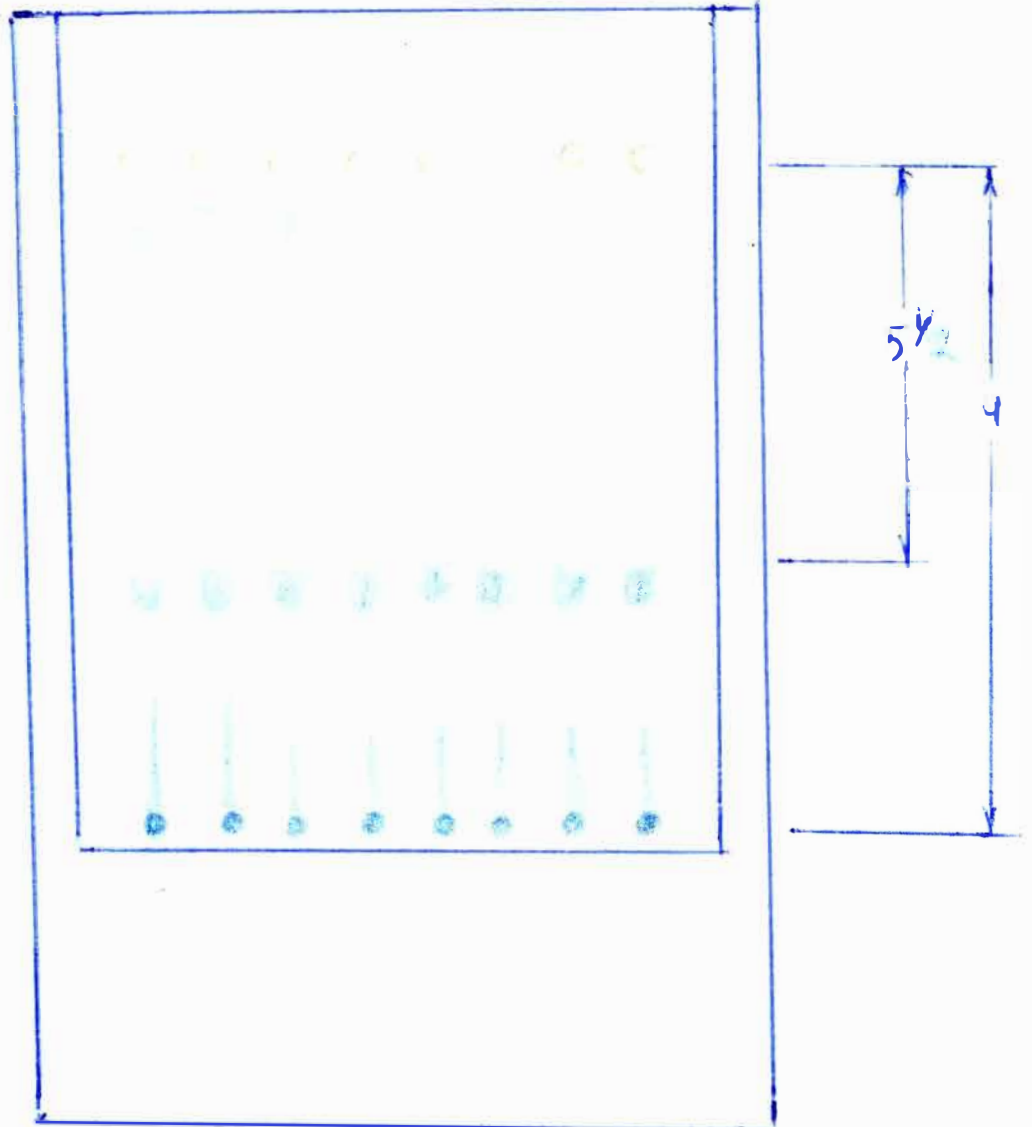
Distance Traveled
(cm.)

Brown

Light green-yellow

Brown-black crescent
Light blue

Dark purple



White Birch Chromatogram II.

Color of Spot

Distance Traveled
(cm.)

Brown

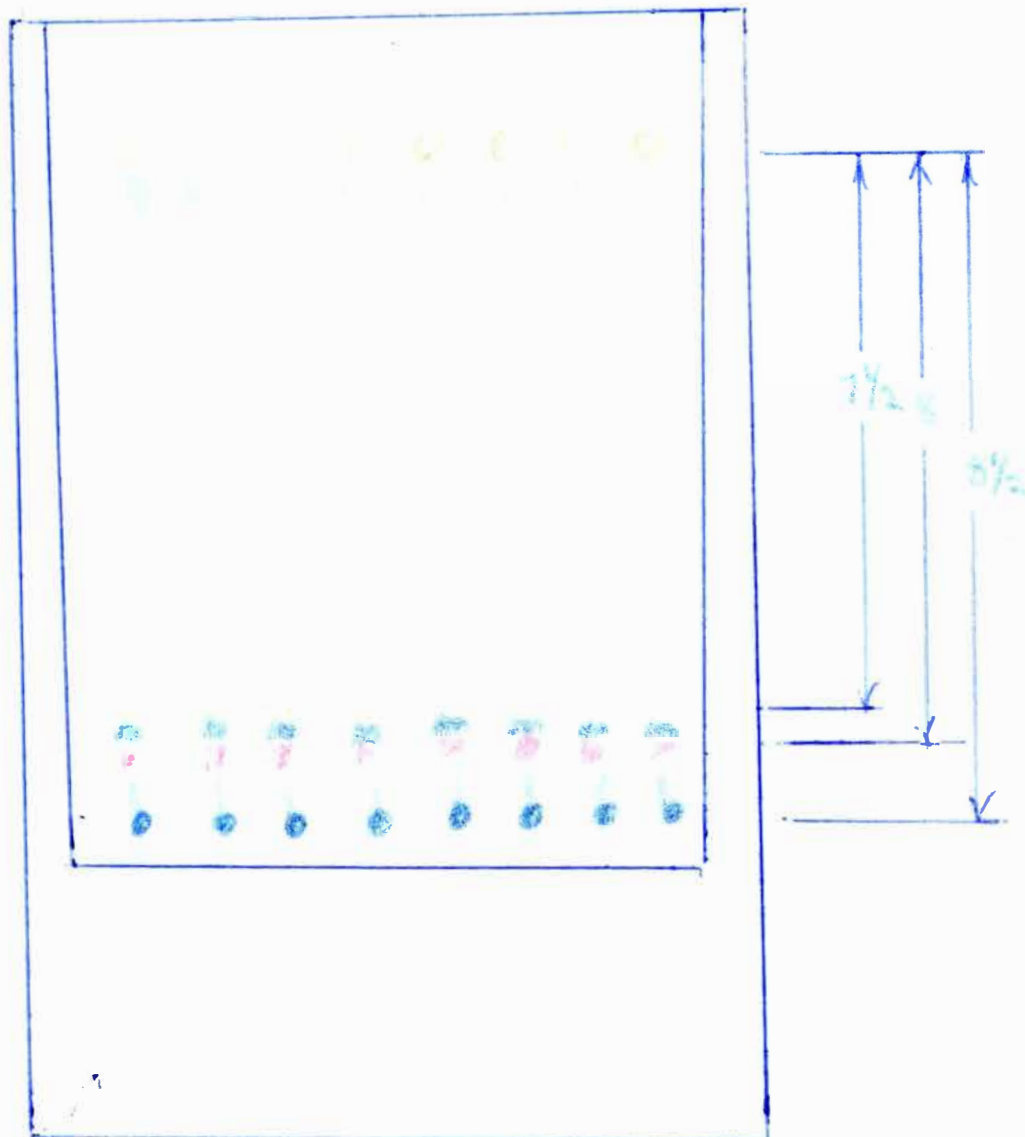
Light green-yellow

Brown-black crescent

Light blue

Violet

Dark purple



DISCUSSION AND CONCLUSION:

As it can be seen from the illustrated chromatograms on the preceding pages good separations of five or six components were obtained on the test spent liquors. The chromatograms of the spent liquors from Hemlock, Hard Maple, and Aspen wood species were in very close agreement in respect to the number of spots obtained, the color of the spots, color intensity of the spots and the distances traveled by the spots. The White Birch, however, showed differences in the distances traveled by spots that were present in the other wood species chromatograms. In addition, the White Birch displayed the presence of a component not present in the other three types. This additional spot appeared as a violet spot in the chromatograms. This result was checked by performing a second cooking process on White Birch chips and subjecting the spent liquor to chromatographic analysis. The same results were observed for the second test, however, the additional component spot wasn't as intense as it was in the first chromatogram of this species.

From the results it may be concluded that the spent liquor from the White Birch wood species contained a major constituent not present in the spent liquors from the other three wood species. Presently, there is no way of telling exactly what the differences are chemically. However, research is underway to ascertain the identity of the component spots appearing on the chromatograms.

References

1. Sulphite Pulp Manufacturer's Research League, Personal Communication.